

Process for improving the stability over time or for enabling the measurement of the electrical conduction properties of a film of active material on an insulating substrate, and conductimetric sensor obtained by this process

DESCRIPTION

Technical field

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The present invention relates to a process for improving the contact between, on the one hand, an insulating substrate provided with thin metal electrodes and, on the other hand, a film of active material having electrical conduction properties.

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The invention applies, in particular, to all fields in which the electrical conduction properties of an organic, metallo-organic or hybrid (organic and mineral) active material, arranged in the form of a thin film on top of an insulating substrate covered with thin metal electrodes are utilized. Among the devices that utilize the electrical conduction properties of a thin film, mention may be made of conductimetric chemical sensors and electronic components of the field-effect transistor type.

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In these devices, the active material is in the form of a thin film produced, for example, by the Langmuir-Blodgett technique, by covalent grafting, by sequential deposition of self-assembled layers, by chemisorption or by any other conventional technique for depositing thin films. This film is deposited on an insulating substrate provided with thin metal electrodes, which make it possible to carry out the conductivity measurement.

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Prior art

A device of this type is, for example, described in reference 1: EP-A-0 251 934. In this device, an
5 insulating fluorine substrate is covered with carbon electrodes and with a film formed from one or more monomolecular layers of an active material constituted by a TCNQ charge transfer complex, a TCNQ salt or a precursor. A measurement of the electrical resistance
10 of the film was carried out via the carbon electrodes with a view to detecting the molecular or ionic species in contact with the film. In order to improve the transfer of the monomolecular layers to the substrate, it is possible to firstly deposit monomolecular layers
15 constituted, for example, of ω -tricosenoic acid.

The problems encountered with this type of device relate to the reproducibility of the conductivity measurements and the stability over time. Specifically,
20 the active materials used in these devices, which are organic, metallo-organic or hybrid compounds having very vast potential applications, must be in the form of very thin films and their use in devices provided with thin contact electrodes is severely limited by the
25 phenomena of instability over time of the device and also by the large scatter of the electrical characteristics recorded from one and the same series of devices. These problems are even more acute when the current densities involved are generally low.

30 Furthermore, in the fields of self-assembly and of grafting of materials based on organic, metallo-organic or hybrid compounds, electrical measurements on such structures positioned on an inserting substrate covered
35 with thin electrodes are, for the moment, in theory impossible to produce.

The objective of the invention is specifically to solve this problem of scatter and of instability over time of

the electrical measurements carried out on such materials and to furthermore allow such measurements to be carried out on self-assembled structures positioned on an insulating substrate provided with metal electrodes.

Summary of the invention

Thus, one subject of the invention is a process for improving the stability over time or for enabling the measurement of the electrical conduction properties of a film of active material placed on an insulating substrate provided, on certain areas of its surface, with metal electrodes, which consists in producing, at the interface between the insulating substrate and the film of active material and at the interface between the electrodes and the film of active material, at least one monomolecular interlayer composed of organic molecules covalently bonded to the substrate or the electrodes, said molecules comprising an organic group capable of improving the mechanical and/or electrical contact properties between the film of active material and the metal electrodes and between the film of active material and the substrate.

According to the invention the interlayer arranged between the substrate and the film of active material allows the nature and quality of the interface produced between the substrate and the film, and between the electrodes and the film, to be controlled. According to the invention, by inserting this interlayer covalently bonded to the substrate and to the electrodes, the surfaces of the substrate and of the electrodes can be rendered identical from the point of view of their physicochemical properties by means of the presence of the organic groups capable of improving the contact with the film of active material. This interlayer thus makes it possible to ensure a more homogeneous deposition of the film of active material onto the

entire surface of the substrate. More specifically, if the two surfaces are physicochemically identical, the discontinuities of the active material in the areas passing from the substrate to the electrodes are appreciably reduced. While, in the case of materials made by spin-coater deposition or by the Langmuir-Blodgett technique, this amounts to an improvement, this point becomes central when it is a matter of making materials by grafting or self-assembly.

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The presence of this interlayer also makes it possible to improve the quality of the mechanical contact between the substrate and the electrodes, on the one hand, and the film of active material, on the other hand.

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Specifically, the differences in the coefficients of expansion between the mineral substrate and an organic or mixed material certainly are partly the cause of difficulties encountered in taking a reliable electrical measurement on organic or mixed materials.

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Finally, the presence of this layer makes it possible to improve the quality of the electrical contact between the substrate and the film of active material.

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This layer may be formed from identical molecules or may comprise different molecules. When it consists of different molecules, these molecules are generally of two types and are arranged in the following manner:

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The first molecules are located at the interface between the substrate and the film of active material, and the second are located at the interface between the metal electrodes and the film of active material.

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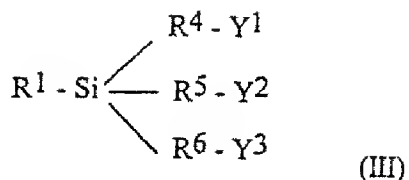
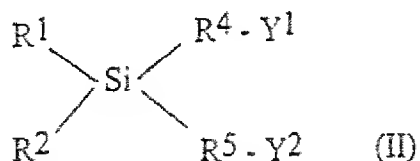
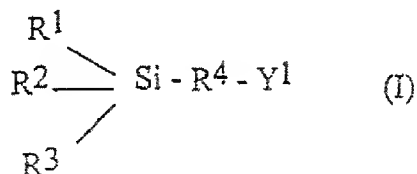
This arrangement makes it possible to take into account the different nature of the insulating substrate and of the metal electrodes in order to establish covalent

bonds between the substrate and the first molecules and between the electrodes and the second molecules.

Generally, the insulating substrate is made of a material comprising silica, for example pure silica, molten silica, quartz or glass, and the first molecules are bonded to the substrate via silicon atoms. In this case, the first molecules may be silane or siloxane derivatives, which have the property of being able to bind via covalent bonding of siloxane type to the substrate.

Generally, the metal electrodes are made of a noble metal, for example gold, platinum or an alloy based on gold or platinum, and covalent bonding may be established between the second molecules and the electrodes, for example via sulphur or nitrogen atoms.

Advantageously, the first molecules correspond to one of the following formulae:



in which:

- R^1 represents a halogen atom or a C_1 to C_4 alkoxy group,
- R^2 and R^3 independently represent a halogen atom, a C_1 to C_4 alkoxy group or a C_1 to C_4 alkyl group;
- 5 - R^4 , R^5 and R^6 independently represent a single bond or linear, aliphatic or aromatic hydrocarbon-based spacer groups, which may contain heteroatoms chosen from O, S and N and/or substituents chosen from amide, amine, ester and urea groups; and
- 10 - Y1, Y2 and Y3 independently represent a hydrogen atom or an organic group chosen from CH_3 , $CH=CH_2$, CN, NCO, NCS, OH, SH, NH_2 , COOH, $CONH_2$, COCl and phenyl, triazole, imidazole and pyridyl groups.
- 15 In these formulae, the alkyl or alkoxy groups used preferably contain one or two carbon atoms.

20 In these formulae, the R^1 group and optionally the R^2 and R^3 groups are leaving groups that allow the attachment of silicon to the substrate. The groups Y1, Y2 and Y3 are groups that improve the contact properties or that allow other reactions.

25 Among the Y groups mentioned are hydrophobic groups (CH_3 , $CH=CH_2$, phenyl), hydrophilic groups (COOH, OH, NH_2 and SH) and groups capable of reacting with the active material, for example by complexation in the case of a pyridyl or triazole group, or by condensation reaction in the case of an NH_2 or COOH group.

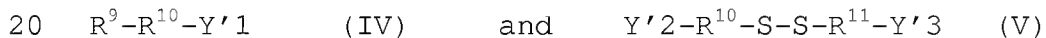
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The choice of the Y1, Y2 and Y3 groups depends in particular on the technique subsequently used for the deposition of the active material. For the Langmuir-Blodgett technique, it is essentially the hydrophilic (Y = OH, SH, NH_2 , etc.) or hydrophobic (Y = CH_3 , $CH=CH_2$, phenyl, etc.) nature that dictates. For covalent
35 grafting and the self-assembly technique, the nature of Y will depend on the type of reaction envisaged. For example, for a condensation reaction with a carboxylic

acid, Y will be an amine; for a complexation on a metal, Y may be a pyridine or a triazole.

When R^1 , R^2 and R^3 represent a chlorine atom and when it is desired to introduce a hydrophilic group into the first molecules of formula I, II or III, it is preferable to use at the start a first molecule in which Y1 represents $CH=CH_2$, and then to chemically modify the molecules by reaction of the allyl group with a reagent capable of introducing a hydrophilic group $COOH$, OH , SH or NH_2 at the end of the chain. Reactions of this type may be performed via the techniques described in reference 2: Wasserman et al., Langmuir, 1989, 5, pages 1074-1087.

The second molecules that are suitable for being attached to the metal electrodes made of noble metal are generally thiol, bisulphide or amine molecules corresponding to the following formulae:



in which:

- R^9 represents SH or NH_2 ,
- R^{10} and R^{11} independently represent a single bond or linear, aliphatic or aromatic hydrocarbon-based spacer groups, which may contain heteroatoms chosen from O, S and N and/or substituents chosen from amide, amine, ester and urea groups; and
- $Y'1$, $Y'2$ and $Y'3$ independently represent a hydrogen atom or an organic group chosen from CH_3 , $CH=CH_2$, CN , NCO , NCS , OH , SH , NH_2 , $COOH$, $CONH_2$, $COCl$ and phenyl, triazole, imidazole and pyridyl groups.

In this case, the attachment of the molecules to the electrodes takes place via S-metal or N-metal bonds.

The choice of molecules corresponding to formulae (IV) and (V) used also depends on the technique that will

subsequently be used for the deposition of the film of active material. Thus, if this material is deposited via the Langmuir-Blodgett technique, the Y' group(s) will be chosen so as to be hydrophilic or hydrophobic.

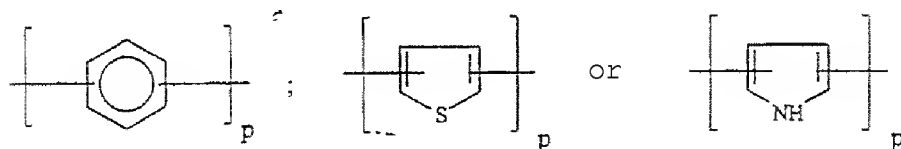
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When the film of the active material is deposited by covalent grafting or by the self-assembly technique, the nature of the Y' groups will depend on the type of reaction envisaged. Thus, if it is desired to perform a
10 condensation reaction between the active material and the interlayer, Y' may be an amine group if the active material comprises a carboxylic acid group. If the reaction envisaged is a complexation reaction on a metal, the Y' group(s) may be a ligand capable of
15 complexing this metal, for example a pyridyl or triazole group.

In formulae (I) to (V) given above, the spacer groups that may be used for R⁴, R⁵, R⁶, R¹⁰ and R¹¹ may in
20 particular be groups of formula (CH₂)_n with n being an integer from 1 to 30 and preferably from 1 to 17.

It is also possible to use groups consisting of oligomers of formulae:

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with p being an integer from 1 to 6,
or aliphatic hydrocarbon-based groups comprising one or
more amide, urea, amine or ester substituents.

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According to a first embodiment of the process of the invention for ensuring the formation of an interlayer composed of two types of molecule, the process comprises the following successive steps:

- a) deposition, onto an insulating substrate comprising silica, of a monomolecular layer of said first organic molecules covalently bonded to the substrate and comprising at least one organic group capable of improving the contact properties with the film of the present invention,
- b) deposition of the flat metal electrodes onto certain areas of the substrate thus treated,
- c) deposition, onto the metal electrodes, of a monomolecular layer of said second molecules covalently bonded to said electrodes and comprising at least one organic group capable of improving the contact properties with the film of active material, and
- d) deposition of the film of active material onto the assembly formed by the substrate and the electrodes thus treated.

In this embodiment of the process of the invention, the first and second molecules may correspond to formulae (I) to (V) given above. When the active material is deposited by the Langmuir-Blodgett technique, the Y and Y' organic groups of the first and second molecules may be different but, preferably, of similar nature to make the surfaces of the substrate and of the electrodes identical from the point of view of their physicochemical properties. These organic groups may be hydrophobic groups or hydrophilic groups. In the case of production of a self-assembled structure, the Y and Y' groups should be identical so as to react with the active material that will subsequently be deposited or with other optional interlayers to form a self-assembled structure via chemical bonds.

The reactions may be of the complexation type, the organic group being, for example, a ligand of the complex, or of the condensation type, for example to form an ester, amide, etc. bond.

According to one variant of this first embodiment of the process of the invention, the first molecules are chosen to promote the adhesion of the metal electrodes made of noble metal to the substrate and to improve the
5 stability over time of the assembly.

In this case, a silane or siloxane substituted with a hydrophilic amine or thiol group is used as first molecules, for example molecules of formula (I), (II)
10 or (III) with the Y group(s) representing an NH_2 or SH group, which are capable of establishing covalent bonds with the electrodes that will be deposited onto the treated substrate.

15 This embodiment of the process of the invention is suitable for the production of a hydrophilic surface state on the insulating substrate and on the metal electrodes.

20 In this variant, the process of the invention comprises the following successive steps:

- a) deposition, onto an insulating substrate comprising silica, of a layer of the first molecules comprising a hydrophilic, for example amine or thiol, groups,
- 25 b) deposition of metal electrodes onto certain areas of the substrate thus treated,
- c) deposition, onto the metal electrodes, of a layer of the second molecules comprising a hydrophilic organic group, chosen, for example, from OH, SH, NH_2
30 and COOH, and
- d) deposition of a film of active material onto the assembly thus treated.

The choice in this process of a silane or siloxane
35 comprising SH or NH_2 groups makes it possible to improve the adhesion of the metal electrodes deposited onto the treated substrate. This improved adhesion property is described in particular in reference 3:

Goss et al., Analytical Chemistry, Vol. 63, No. 1, 1991, pages 85 to 88.

- The molecules used in this implementation variant of the first embodiment of the invention may correspond to the abovementioned formulae (I) to (V) with the Y group(s) representing NH_2 or SH and the Y' group(s) representing OH, COOH, NH_2 or SH.
- According to a second embodiment of the process of the invention, an interlayer consisting of only one type of molecule is attached to the substrate and to the electrodes by performing the following successive steps:
- a') deposition, onto an insulating substrate comprising silica, of a layer of silane or siloxane substituted with an amine or thiol group, which acts as promoter for the adhesion of the metal electrodes to the substrate,
 - b') deposition of the metal electrodes to certain areas of the substrate thus treated,
 - c') deposition, onto the metal electrodes, of a layer of organic molecules linked to the electrodes via sulphur or nitrogen atoms,
 - d') oxidation of the assembly with ozone to remove the organic molecules on the substrate and the electrodes,
 - e') deposition, onto the assembly, of a monomolecular layer of organic silane or siloxane molecules comprising an organic group capable of improving the contact properties with the film of active material, and
 - f') deposition of the film of active material onto the assembly thus treated.
- In step a') of this process, the organic molecules used to improve the adhesion of the metal electrodes to the substrate may correspond to the abovementioned formulae (I) to (III).

In step c') of this process, organic molecules of the thiol, amine or bisulphide type such as the molecules corresponding to formula (IV) or (V) are deposited onto the electrodes, as in the embodiments described above, and the assembly is then subjected to an oxidation treatment with ozone, which has the effect of destroying the organic molecules. In the following step e'), it is, however, possible to deposit, not only onto the insulating substrate, but also onto the metal electrodes, organic molecules consisting of silanes or siloxanes and to establish covalent bonds not only between these molecules and the substrate, but also between these molecules and the electrodes.

Molecules of formula (I), (II) or (III) may also be used in step e') to obtain a uniform surface finish on the substrate and the electrodes.

It is assumed that the deposition of silane or siloxane onto the metal electrodes is made possible by the preceding oxidation treatment, after formation of a covalent bond with sulphur or nitrogen atoms.

This second embodiment of the process of the invention is suitable in particular for making self-assembled structures, since chemical bonds may be established between the molecules deposited during step e') and an active material whose electrical properties it is desired to measure.

To perform the process of the invention, the steps of deposition of silane or siloxane onto the insulating substrate may be performed via standard methods such as those described in reference 3 mentioned above and references 4 and 5: Brzoska et al., Nature, Vol. 360, 1992, pages 719-721, and McGovern et al., Langmuir, 1994, Vol. 10, No. 10, pages 3607-3614.

This generally consists in immersing the substrate in a solution of the silane or siloxane in a suitable solvent. This solvent is preferably apolar, for example toluene in the case of silanes. The temperature used
5 depends on the silane or siloxane used.

The deposition of the metal electrodes may also be performed via standard techniques such as those usually used for making thin electrodes, for example vacuum
10 evaporation or cathodic sputtering.

The deposition of molecules of the thiol, disulphide or amine type may be performed by using the standard techniques described in reference 6: Bain et al., Am.
15 Chem. Soc., 1989, 111, pages 321-335.

In the last step of the process, it is possible to use various active materials, for example amphiphilic compounds capable of being deposited by the Langmuir-
20 Blodgett technique such as amphiphilic charge-transfer complexes, TCNQ complexes, ethylene-dithiotetrathiofulvalenes (EDF-TTF), porphyrins, porphyrazines, or more generally any material capable of having
25 electrical conduction properties. This deposition may also be carried out by other techniques, for example by covalent grafting, by sequential deposition of self-assembled layers, by spincoating, by duplication, etc.

Other features and advantages of the invention will
30 appear more clearly on reading the following description of exemplary embodiments given, of course, by way of illustration and non-limitingly.

Brief description of the drawings

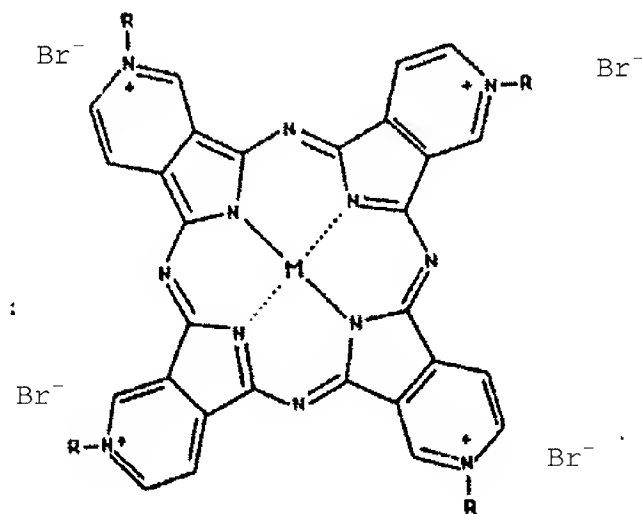
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Figure 1 is a schematic vertical cross-sectional representation of a conductimetric sensor obtained by the process of the invention;

Figure 2 is a histogram representing the resistance of

10 identical sensors according to the invention;
Figure 3 illustrates, by way of comparison, the results
obtained in the case of 10 identical sensors that do
not comprise the interlayer of the invention;
5 Figure 4 is a diagram representing the electrical
resistance measurements carried out on 4 samples as a
function of the time in days; and
Figure 5 illustrates the results obtained under the
same conditions on 6 different samples that do not
10 comprise interlayers as in the invention.

The following examples illustrate the manufacture of
sensors according to the invention, starting from a
glass substrate that is 1 cm wide by 3.5 cm long, and
15 using an active material constituted by an amphiphilic
tetrapyrridino-phthalocyanine corresponding to the
following formula:



20 in which R represents the octadecyl group and M
represents Cu.

Example 1

25 In this example, the first embodiment of the invention
is followed, by performing the following steps:

1) Silanization of the substrate

The molecule used for this silanization is octadecyltrichlorosilane.

5

First, the substrate is carefully cleaned with basic soap and is then rinsed 10 times with demineralized water. It is then made hydrophilic by treatment in a piranha solution, which is a mixture of aqueous hydrogen peroxide and of sulphuric acid in a 3:7 ratio by volume, at a temperature of 150°C for 1 hour, and is then rinsed 10 times with demineralized water and dried under nitrogen in an oven at 100°C.

15 The substrate thus treated is then dipped into a solution containing 10^{-3} mol/l of octadecyltrichlorosilane in toluene, for 30 minutes at room temperature.

A substrate modified with a layer of molecules comprising hydrophobic end groups is thus obtained.

2) Deposition of the gold electrodes

This is performed via the standard vacuum evaporation techniques and interdigitated gold electrodes 500 Å thick, formed from 20 combs 5 mm long and 150 µm wide, separated by 150 µm, are thus deposited.

3) Functionalization of the electrodes

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In this step, dodecanethiol is deposited onto the gold electrodes. This is performed by dipping the substrate covered with the electrodes into a 10^{-3} mol/l solution of dodecanethiol in ethanol, for 12 hours, at room temperature. Bonding of the molecules with the gold electrodes is thus obtained, these molecules comprising a hydrophobic end group, for instance the silane previously attached to the substrate.

4) Deposition of the film active material

The deposition of this material is performed by the Langmuir-Blodgett technique, as described in reference
5 7: Palacin S. and Barraud A., 1991, Colloids and Surfaces, 52, pages 123-146. 10 layers are thus deposited to obtain a thickness of 200 Å.

Figure 1 illustrates, in vertical cross section, the
10 sensor thus obtained.

Seen in this figure is the glass substrate 1 covered with the layer 3 of the first octadecyltrichlorosilane molecules and with the gold electrode 5. This electrode
15 is itself covered with the layer 7 of dodecanethiol and with the film 9 of the active material that covers the assembly.

A sensor according to the prior art would not comprise
20 layers 3 and 7.

The electrical resistance of the film of active material is then determined for the 10 sensors prepared in an identical manner by applying, between the
25 electrodes, a voltage of 1 volt, in air and at room temperature.

The results obtained are given in Figure 2. In this figure, it is seen that out of the 10 samples tested, 5
30 have a resistance of 1.5×10^9 ohms, 3 have a resistance of 1×10^9 ohms, and 2 have a resistance of 2×10^9 ohms.

The scatter of the results is therefore small.

35

In Figure 3, the results obtained with a substrate identical to that from Example 1 covered with gold electrodes as in Example 1 and with a film of active material identical to that from Example 1 but without

the interlayer (7) is represented by way of comparison.

Figure 3 represents the results obtained. In this figure, it is seen that the 3 samples have a resistance of 3×10^9 ohms and that the other samples are distributed over lower values for 4 samples and higher values for 3 samples. The scatter of the results is therefore very large relative to what is obtained with the invention.

10

Example 2

In this example, the variant of the first embodiment of the invention is followed, to obtain a layer containing hydrophilic end groups.

In this case, the substrate is prepared as in Example 1, and a layer of (3-mercaptopropyl)trimethoxysilane is then deposited thereon by following the procedure described by Goss et al. in reference 3: Analytical Chemistry, 1991, 63, pages 85-88.

To this end, the substrate is dipped into a solution consisting of 400 g of propanol and 10 g of water containing 10 g of (3-mercaptopropyl)trimethoxysilane.

Gold electrodes are then deposited onto the substrate thus treated by working as in Example 1, and these electrodes are then coated with a layer of bis-(2-hydroxyethyl) disulphide by immersing the substrate in a 10^{-3} mol/l solution of this disulphide in ethanol, for about 24 hours at a temperature in the region of 20°C. A substrate comprising hydrophilic (thiol) end groups and electrodes also comprising hydrophilic end (OH) groups is thus obtained.

The substrate thus treated may be used to make the deposit of the film of active material by following the same procedure as in Example 1.

In this way four samples are produced and the resistance of each of them is determined as a function of time (in days). The results obtained are given in
5 Figure 4 which represents the change in R/R_0 as a function of time (in days). R is the resistance at time t and R_0 is the initial resistance.

In this figure only one single curve is seen, which
10 curve corresponds to the four samples tested. They therefore all behave in the same way with a small drift as a function of time.

In Figure 5, the results for the same test carried out
15 on six samples that had not undergone the treatment of the invention in order to produce an interlayer between the substrate, the electrodes and the film of active material are represented by way of comparison.

20 In this case, it is observed that the six samples behave differently (curves 1 to 6) and that the variations in the resistance are very large as a function of time.

25 It is clear that the production, in accordance with the invention, of an interlayer covalently bonded to the substrate and to the electrodes and comprising hydrophilic surface groups considerably improves the stability of the sensor as a function of time.

30

Example 3

In this example, the second embodiment of the invention is followed, i.e. an additional oxidation step is
35 performed, after modification of the substrate and of the electrodes, respectively, with a silane and with a thiol, and a layer of dodecanethiol is then deposited onto the assembly.

The first steps of the process consist in treating the substrate and then in depositing the metal electrodes and functionalizing the metal electrodes by using for the silanization of the substrate (3-mercaptopropyl)-
5 trimethoxysilane as in Example 2, and then modifying the electrodes with dodecanethiol, as in Example 1. A substrate coated with silane molecules comprising at the surface an SH group and gold electrodes coated with dodecanethiol is thus obtained.

10 An oxidation with ozone is then performed, this oxidation being performed in apparatus that forms ozone by UV irradiation using oxygen, for half an hour. Under these conditions, the hydrocarbon-based chains of the
15 previously deposited organic compounds are destroyed and a deposition of silane may then be performed on the substrate and electrode assembly, the silanization being performed with octadecyltrichlorosilane, as in Example 1.

20 It is then found that the surface of the electrodes, like the surface of the substrate, shows poor properties of wettability with water, the contact angle with water being 115° on glass and 110° on gold. This
25 result confirms that a homogeneous modification of the entire surface of the substrate with the octadecyltrichlorosilane has been obtained.

Example 4

30 This example illustrates the production of a hybrid self-assembled structure on which it is possible to measure an electrical conductivity.

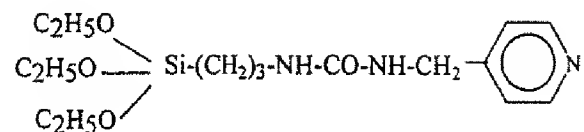
35 For this purpose, the second embodiment of the invention is used and the procedure from Example 2 is followed in order to deposit, on the glass substrate from Example 1, a layer of (3-mercaptopropyl)trimethoxysilane, then gold electrodes and a layer of

bis(2-hydroxyethyl) disulphide.

An oxidation of the assembly with ozone, as in Example 3, is then carried out.

5

After this oxidation, a layer of a siloxane of formula:



10 is deposited on the assembly by immersing in a 10^{-3} mol/l solution of this compound in anhydrous toluene, for 24 hours.

This compound, 1-(3-(triethoxysilyl)propyl)-
15 3-(pyridine-4-methyl)urea, was synthesized as follows.

Added to a solution of 1 ml of 4-methylaminopyridine (0.01 mol) in 15 ml of anhydrous chloroform are 2.5 ml of 3-isocyanatopropyltriethoxysilane (0.01 mol). The
20 reaction is carried out at normal temperature, with stirring and under a nitrogen atmosphere, for 5 hours. The solvent is removed under vacuum and the crude solid is recrystallized several times at low temperature in diethyl ether.

25

A phthalocyanine or a porphyrin comprising, at its centre, a metal that can be complexed by pyridine is then deposited by immersing the assembly in a 10^{-3} M solution of phthalocyanine or porphyrin for 6 hours.

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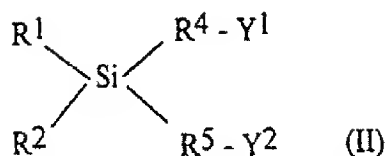
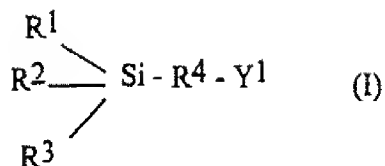
It is thus possible to determine the electrical characteristics of the self-assembled structure on the substrate provided with its electrodes.

REFERENCES

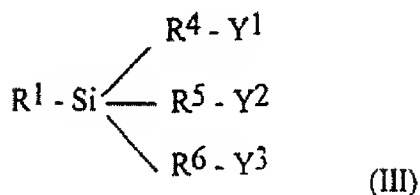
- Reference 1: EP-A-0 251 934.
- 5 Reference 2: Wasserman et al., Langmuir, 1989, 5,
pages 1074-1087.
- Reference 3: Goss et al., Analytical Chemistry,
Vol. 63, No. 1, 1991, pages 85-88.
- 10 Reference 4: Brzoska et al., Nature, Vol. 360, 1992,
pages 719-721.
- Reference 5: McGovern et al., Langmuir, 1994,
15 Vol. 10, No. 10, pages 3607-3614.
- Reference 6: Bain et al., Am. chem.. Soc., 1989, 111,
pages 321-335.
- 20 Reference 7: Palacin S, Barraud A., 1991, Colloids
and Surfaces, Vol. 52, pages 123-146.

CLAIMS

1. Process for improving the stability over time or for enabling the measurement of the electrical conduction properties of a film of active material deposited on an insulating substrate provided, on certain areas of its surface, with metal electrodes, characterized in that it consists in producing, at the interface between the insulating substrate and the film of active material and at the interface between the electrodes and the film of active material, at least one interlayer composed of organic molecules covalently bonded to the substrate or the electrodes, said molecules comprising an organic group capable of improving the mechanical and/or electrical contact properties between the film of active material and the metal electrodes and between the film of active material and the substrate.
2. Process according to Claim 1, in which the molecules of the interlayer located at the interface between the substrate and the film of active material, known as first molecules, are different from the molecules of the interlayer that are located at the interface between the metal electrodes and the film of active material, known as second molecules.
3. Process according to Claim 2, in which said first molecules are bonded to the insulating substrate via silicon atoms, and the second molecules are bonded to the electrodes via sulphur or nitrogen atoms.
4. Process according to Claim 3, in which the first molecules respond to one of the following formulae:



:



in which

- 5 - R^1 represents a halogen atom or a C_1 to C_4 alkoxy group;
- R^2 and R^3 independently represent a halogen atom, a C_1 to C_4 alkoxy group or a C_1 to C_4 alkyl group;
- 10 - R^4 , R^5 and R^6 independently represent a single bond or linear, aliphatic or aromatic hydrocarbon-based spacer groups, which may contain heteroatoms chosen from O, S and N and/or substituents chosen from amide, ester, amine and urea groups; and
- 15 - Y^1 , Y^2 and Y^3 independently represent a hydrogen atom or an organic group chosen from CH_3 , $\text{CH}=\text{CH}_2$, CN, NCO, NCS, OH, SH, NH_2 , COOH, CONH_2 , COCl, and phenol, triazole, imidazole and pyridyl groups.

20

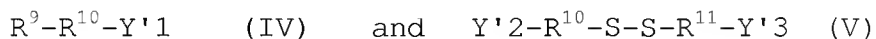
5. Process according to Claim 4, in which the first molecules correspond to the formula (I) with R^1 , R^2 and R^3 representing a chlorine atom and Y^1 representing $\text{CH}=\text{CH}_2$, and in which the organic

molecules deposited on the substrate are then chemically modified by reaction of the $\text{CH}=\text{CH}_2$ group with a reactant capable of introducing, at the end of the chain, an OH, SH or NH_2 group.

5

6. Process according to any one of Claims 3 to 5, in which said second molecules are thiol, bisulphide or amine molecules corresponding to one of the following formulae:

10



in which:

- 15 - R^9 represents SH or NH_2 ;
- R^{10} and R^{11} independently represent a single bond or linear, aliphatic or aromatic hydrocarbon-based spacer groups, which may contain heteroatoms chosen from O, S and N and/or substituents chosen from amide, ester, amine and urea groups; and
20 - $\text{Y}'1$, $\text{Y}'2$ and $\text{Y}'3$ independently represent a hydrogen atom or an organic group chosen from CH_3 , $\text{CH}=\text{CH}_2$, CN, NCO, NCS, OH, SH, NH_2 , COOH, CONH_2 , COCl, and phenol, triazole, imidazole and pyridyl groups.

25

7. Process according to Claim 4 or 6, in which R^4 , R^5 , R^6 , R^{10} and/or R^{11} represent a group of formula $(\text{CH}_2)_n$ with n being an integer from 1 to 30.

30

8. Process according to any one of Claims 2 to 7, comprising the following successive steps:

35

- a) deposition, onto an insulating substrate comprising silica, of a monomolecular layer of said first organic molecules covalently bonded to the substrate and comprising at least one organic group capable of improving the contact properties with the film of active material;
b) deposition of the flat metal electrodes onto certain areas of the substrate thus treated;

c) deposition, onto the metal electrodes, of a monomolecular layer of said second molecules covalently bonded to said electrode and comprising at least one organic group capable of improving the contact properties with the film of active material; and

d) deposition of the film of active material and the assembly formed by the substrate and the electrodes thus treated.

10

9. Process according to any one of Claims 2 to 7, comprising the following successive steps:

a) deposition, onto an insulating substrate comprising silica, of a layer of the first molecules comprising a hydrophilic group in order to promote the adhesion of the electrodes to the substrate;

b) deposition of the metal electrodes onto certain areas of the substrate thus treated;

c) deposition, onto the metal electrodes, of a layer of the second molecules comprising a hydrophilic organic group; and

d) deposition of a film of active material onto the assembly thus treated.

25

10. Process according to Claim 1, comprising the following successive steps:

a') deposition, onto an insulating substrate comprising silica, of a layer of silane or siloxane substituted by an amine or thiol group, which acts as promoter for the adhesion of the metal electrodes to the substrate;

b') deposition of the metal electrodes to certain areas of the substrate thus treated;

c') deposition, onto the metal electrodes, of a layer of organic molecules bonded to the electrodes by sulphur or nitrogen atom;

d') oxidation of the assembly with ozone to remove the organic molecules on the substrate and

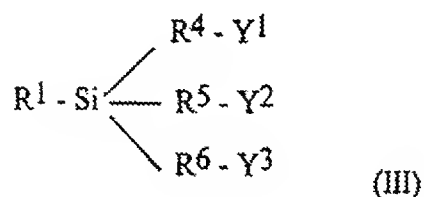
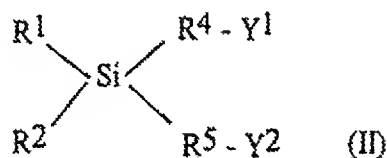
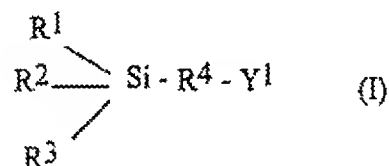
35

the electrodes;

e') deposition, onto the assembly, of a monomolecular layer of organic silane or siloxane molecules comprising an organic group capable of improving the contact properties with the film of active material; and

f') deposition of the film of active material onto the assembly thus treated.

11. Process according to Claim 10, in which the molecules used in step a') and e') correspond to one of the following formulae:



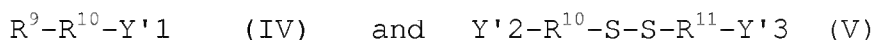
in which

- R^1 represents a halogen atom or a C_1 to C_4 alkoxy group;
- R^2 and R^3 independently represent a halogen atom, a C_1 to C_4 alkoxy group or a C_1 to C_4 alkyl group;
- R^4 , R^5 and R^6 independently represent a single bond or linear, aliphatic or aromatic hydrocarbon-

based spacer groups, which may contain heteroatoms chosen from O, S and N and/or substituents chosen from amide, ester, amine and urea groups; and

5 - Y1, Y2 and Y3 independently represent a hydrogen atom or an organic group chosen from CH₃, CH=CH₂, CN, NCO, NCS, OH, SH, NH₂, COOH, CONH₂, COCl, and phenol, triazole, imidazole and pyridyl groups.

10 12. Process according to either one of claims 10 and 11, in which the molecules used in step c') correspond to one of the following formulae:



in which:

 - R⁹ represents SH or NH₂;
 - R¹⁰ and R¹¹ independently represent a single bond or linear, aliphatic or aromatic hydrocarbon-based spacer groups, which may contain heteroatoms chosen from O, S and N and/or substituents chosen from amide, ester, amine and urea groups; and
20 - Y'1, Y'2 and Y'3 independently represent a hydrogen atom or an organic group chosen from CH₃,
25 CH=CH₂, CN, NCO, NCS, OH, SH, NH₂, COOH, CONH₂, COCl, and phenol, triazole, imidazole and pyridyl groups.

30 13. Process according to Claim 10, in which the organic molecules used in step a') are (3-mercaptopropyl)trimethoxysilane molecules, the molecules used in step c') are bis(2-hydroxyethyl) disulphide molecules and the molecules used in step e') are octadecyltrichlorosilane or
35 1-(3-(triethoxysilyl)propyl)-3-(pyridine-4-methyl)urea molecules.

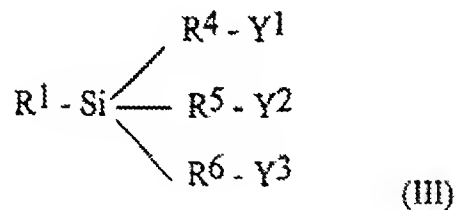
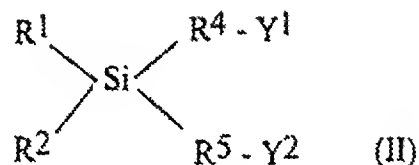
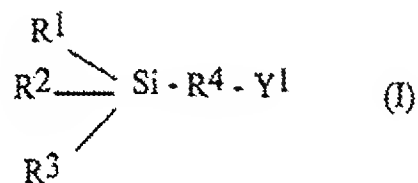
14. Process according to Claim 8, in which the first molecules are octadecyltrichlorosilane molecules

and the second molecules are dodecanethiol molecules.

15. Process according to Claim 9, in which the first
5 molecules are (3-mercaptopropyl)trimethoxysilane molecules and the second molecules are bis-(2-hydroxyethyl) disulphide molecules.
16. Process according to any one of Claims 1 to 15, in
10 which the active material is an amphiphilic porphyrin.
17. Conductimetric sensor comprising an insulating
15 substrate provided on certain areas of its surface with thin metal electrodes uncovered with a film of organic or organomineral active material, in contact with the substrate and with the electrodes, characterized in that it comprises, in addition, at the interface between the substrate
20 and the film of active material and at the interface between the electrodes and the film of active material, at least one monomolecular interlayer constituted of organic molecules covalently bonded to the substrate or to the electrodes, said molecules comprising an organic
25 group that improves the mechanical and/or electrical contact properties between the film of active material and the metal electrodes and between the film of active material and the substrate.
30
18. Sensor according to Claim 17, in which the organic
35 group of the molecules of the interlayer is chosen from hydrophilic groups, hydrophobic groups and groups that form a chemical bond with the active material.
19. Sensor according to Claim 17 or 18, in which the molecules of the interlayer located at the

interface between the substrate and the film of active material, known as first molecules, are different from the molecules of the interlayer that are located at the interface between the metal electrodes and the film of active material, known as second molecules.

20. Sensor according to Claim 19, in which the first molecules respond to one of the following formulae:



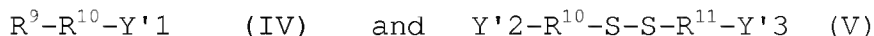
in which

- R^1 represents a halogen atom or a C_1 to C_4 alkoxy group;
- R^2 and R^3 independently represent a halogen atom, a C_1 to C_4 alkoxy group or a C_1 to C_4 alkyl group;
- R^4 , R^5 and R^6 independently represent a single bond or linear, aliphatic or aromatic hydrocarbon-based spacer groups, which may contain heteroatoms

chosen from O, S and N and/or substituents chosen from amide, ester, amine and urea groups; and

5 - Y1, Y2 and Y3 independently represent a hydrogen atom or an organic group chosen from CH₃, CH=CH₂, CN, NCO, NCS, OH, SH, NH₂, COOH, CONH₂, COCl, and phenol, triazole, imidazole and pyridyl groups.

10 21. Sensor according to Claim 19 or 20, in which the second molecules corresponding to one of the following formulae:



15 in which:

- R⁹ represents SH or NH₂;
- R¹⁰ and R¹¹ independently represent a single bond or linear, aliphatic or aromatic hydrocarbon-based spacer groups, which may contain heteroatoms
20 chosen from O, S and N and/or substituents chosen from amide, ester, amine and urea groups; and
- Y'1, Y'2 and Y'3 independently represent a hydrogen atom or an organic group chosen from CH₃, CH=CH₂, CN, NCO, NCS, OH, SH, NH₂, COOH, CONH₂,
25 COCl, and phenol, triazole, imidazole and pyridyl groups.

30 22. Sensor according to any one of Claims 17 to 21, in which the substrate is a silica-based material and the electrodes are made of a noble metal.

35 23. Self-assembled structures comprising an insulating substrate provided on certain areas of its surface with thin metal electrodes, the assembly being covered with an interlayer of molecules capable of establishing chemical bonds, on the one hand, with the electrodes and the substrate and, on the other hand, with an active material.

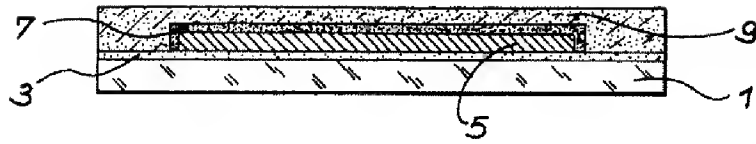


FIG. 1

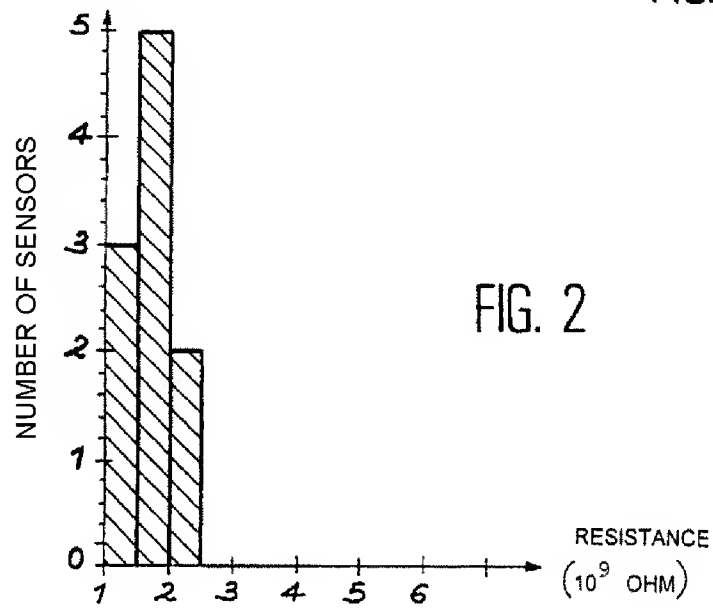


FIG. 2

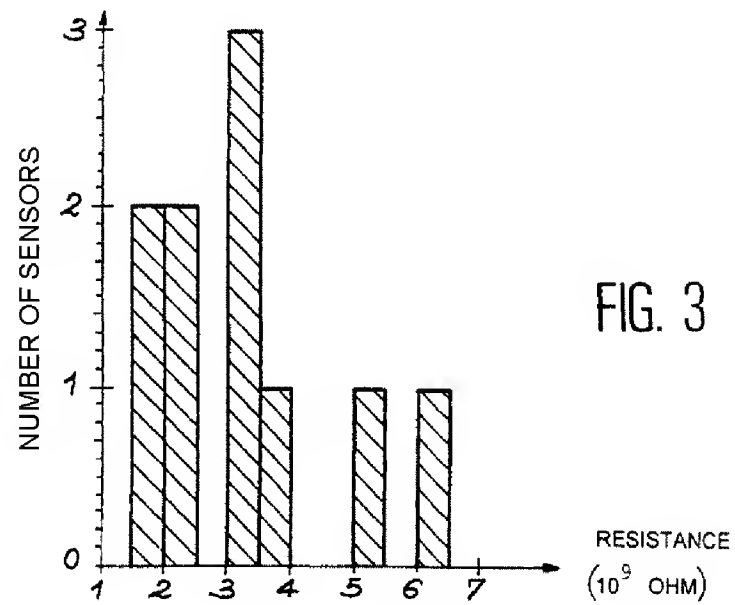


FIG. 3

